

RIG TECHNIQUES AND EXPERIMENTS

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ABSTRACT

Experimental investigations utilising laboratory test rigs have played a major role in advancing the concept of CO₂ ocean storage. These types of experiments are anticipated to remain an important component of this research and development endeavor. The present paper reviews past and ongoing laboratory studies and offers some recommendations for future work. In the near-term, high priority should be assigned to investigations of: (1) buoyant droplet plumes in stratified media; (2) CO₂ injection dynamics; and (3) multiple droplet interaction phenomena. The development of robust instruments that can be used to monitor scalars and velocities in a field disposal test must also be pursued and studies of hydrate fouling of pipelines and injectors should be initiated.

INTRODUCTION

While utilisation of the deep ocean as a long-term repository for fossil carbon is attractive in concept, the effectiveness and technical feasibility of this approach to stabilize atmospheric CO₂ levels have not been substantiated. Economic considerations notwithstanding, the viability of ocean containment will depend primarily upon devising appropriate disposal methods that will promote long residence times while minimising disruptions to marine biota.

Over the past decade, efforts have intensified to model the behavior of CO₂ oceanic discharges in order to predict the period of containment and to quantify perturbations to the marine environment. The first two workshops of this series examined the status of these activities (Ormerod, 1996; Ormerod and Angel, 1996). While insight has been gained, it also has become clear that, at present, predictive calculations suffer in varying degrees from a lack of data necessary for model development and calibration. Experiments are therefore an indispensable component of the CO₂ ocean storage development strategy. The primary role of experimental investigations, however, is not to support advances in modelling but rather to elucidate fundamental phenomena which occur when CO₂ is injected into the deep ocean.

There are four general categories of experiments which warrant effort in the near-term: (1) laboratory-scale investigations that examine specific physical processes in high-pressure sea water-CO₂ systems; or develop and test diagnostics for field applications; (2) pilot-scale field tests which provide operational information on prototypical disposal systems and monitor CO₂ transport and changes in sea water chemistry in the near-field of the discharge (order of metres to kilometres) over short time-scales (order of hours to weeks); (3) tracer experiments to investigate long length- and time-scale advective/diffusive mixing phenomena; and (4) biological studies, conducted either *in situ* or *ex situ*, that assess the response of individual marine organisms or ecosystems exposed to concentrated CO₂ discharges. Tracer experiments of type (3) complement ongoing mesoscale and ocean general circulation modelling (OGCM) efforts, providing vital information on eddy diffusivities and turnover phenomena. As typically conducted, these experiments are more relevant to estimating the term of sequestration than to assessing local environmental impacts or to engineer disposal systems. Environmental and engineering issues are addressed by the laboratory, field disposal, and biological investigations.

The objective of this paper is to review the progress of laboratory-scale (i.e., rig) studies of the CO₂ ocean storage concept and to identify experiments which are needed to advance successfully toward implementation. Laboratory investigations of the response and mortality of affected biota are not considered.

LABORATORY EXPERIMENTS

Laboratory rig experiments provide the obvious benefit, when properly planned and executed, of allowing individual phenomena to be isolated and examined under well-controlled conditions. Their principal shortcoming lies in being unable to simulate fully the complex coupling of processes which may take place in the field. Furthermore, with regard to CO₂ discharges in the deep ocean, transport occurring at long length- and time-scales is impossible to replicate properly within the restrictive confines of a test rig. Laboratory studies are therefore more effectively applied to investigate near-field effects and to resolve engineering and operational concerns.

The role of rig experiments at the current state of development of CO₂ ocean storage includes:

1. Validation of Principles of Operation of Disposal Techniques—Rig experiments are the primary vehicle for initial assessments of the viability of proposed disposal methods. For example, some early conceptual studies of deep ocean sequestration (Golomb *et al.*, 1989; Saji *et al.*, 1992; Austvik & Løken, 1992; Golomb *et al.*, 1992) speculated that direct discharge of CO₂ might generate *in situ* dense clathrate hydrates that would sink and deposit on the seabed. It was hoped that the solid phase would isolate the fossil carbon from the sea water and inhibit back-transport to the atmosphere. Subsequent laboratory investigations, however, revealed that wholesale conversion of a CO₂ effluent flow to hydrates was unlikely (Masutani *et al.*, 1993; Holder & Warzinski, 1996) and that the hydrates which form are unstable and rapidly dissolve upon exposure to sea water undersaturated with CO₂ (North *et al.*, 1993; Aya *et al.*, 1993).

Fundamental information on the behavior of CO₂ discharges in high-pressure seawater is still emerging from laboratory studies. Enhanced understanding of basic phenomena should give rise to innovative strategies to sequester CO₂ in the ocean.

2. Support Near-Field Modelling Efforts—Changes in sea water chemistry in the region immediately adjacent to the release point must be quantified in order to evaluate environmental impacts. Present generation OGCMs and many mesoscale models are unable to resolve details of the very near-field (limiting horizontal resolution is about 100 km for OGCMs and 10 km for mesoscale models). Work recently has been initiated on local models that incorporate fine-scale processes (Liro *et al.*, 1992; Drange *et al.*, 1993; Caulfield *et al.*, 1997; Dewey *et al.*, 1997). Rig experiments will both support and drive these efforts, by providing data for calibration/validation and suggesting new modelling approaches as details of the physics of candidate discharge processes are clarified.
3. Process Simulation—For a selected disposal scenario (e.g., direct release of pure CO₂; CO₂-enriched sea water effluent discharges), scaled-down process simulations can be conducted in the laboratory to anticipate problems arising from off-design operation and transients; and to engineer solutions to these problems. These tests will examine the performance of individual components such as injectors or conduits during start-up, shut-down, and under partial load. Field experiments ultimately must be performed to evaluate the operation of integrated systems.
4. Planning Field Experiments—Modelling and laboratory studies are no longer sufficient to sustain development of the CO₂ ocean storage option. A pilot scale field test must be conducted in the near future. Such an undertaking will require a significant investment of resources and will be subject to the relatively high level of risk characteristic of ocean

experimentation. The results of rig experiments can be applied to design equipment, identify areas of focus, and devise test plans and protocols for field studies, potentially reducing both expense and risk and enhancing the probability of their success. Instrument development and characterisation also should be performed, as far as possible, under controlled laboratory conditions prior to transferal to the field.

5. Diagnostic Development—Diagnostics employed in conventional oceanographic research and applications may need to be modified or recalibrated and tested to meet the requirements of CO₂ disposal field tests and eventual full- or pilot-scale process monitoring. Innovative measurement techniques, such as those with the capability to monitor velocity and contaminant concentrations simultaneously (to generate scalar-velocity correlation statistics) or to map the instantaneous velocity or concentration fields, could expand the range of information extracted from both field and laboratory experiments. These types of development activities are pursued primarily in the laboratory, utilizing various test rigs to simulate conditions in the ocean.

To date, the majority of laboratory investigations have concentrated on establishing a qualitative understanding of the phenomenology of CO₂ in contact with high-pressure sea water. While this approach is reasonable at the early conceptual stage of development, it is essential that more effort be directed hereafter to support model development, field testing, and systems engineering. Additional quantitative data will need to be collected, evaluated, and correlated to facilitate these activities.

The following sections provide a brief assessment of past and ongoing laboratory studies and offer some recommendations for the immediate future.

CO₂ Hydrates

Research on CO₂ clathrate hydrates, which are encountered occasionally in nature, predates the current interest in ocean storage of CO₂. Until this idea took hold, however, there was little practical motivation (aside from a few proposals (Williams, 1961; Vlahakis *et al.*, 1972) to use CO₂ hydrates for desalination), to expand on these early equilibrium studies. As mentioned previously, hydrates were first perceived positively as a possible medium to bind fossil carbon emissions, or as a barrier which would forestall transport from deep CO₂ 'lakes' back to the atmosphere and limit local acidification (Shindo *et al.*, 1995). Currently, hydrates are more likely to be viewed as a hindrance, since they can impede dissolution of buoyant CO₂ effluent in sea water at intermediate depths and have the potential to foul and erode disposal conduits and injectors.

The significance of CO₂ hydrates to oceanic containment strategies is reflected in the fact that most related laboratory studies have been undertaken either completely or in part to investigate these substances. Since there was a reasonable amount of information already available on CO₂ hydrate structure and thermodynamics, the emphasis in these studies has been placed on formation kinetics (North *et al.*, 1993; Holder & Warzinski, 1996), stability (North *et al.*, 1993; Fujioka *et al.*, 1994; Aya *et al.*, 1993; Uchida *et al.*, 1997), and material properties such as tensile strength (Aya *et al.*, 1993).

Although still incomplete, the level of understanding of CO₂ hydrates has been elevated significantly as a result of recent laboratory investigations. It is now generally accepted that: (1) hydrates form rapidly (on the order of a second) at the CO₂-sea water interface; (2) the hydrate layer initially is very thin (10s of microns); (3) once formed, the layer impedes but does not stop mass transfer between the CO₂ and water phases; (4) the predominant direction of mass transfer is from the CO₂ to the water phase; penetration of polar water molecules into non-polar liquid CO₂ is unlikely; and (5) the hydrate phase is unstable in water undersaturated with CO₂ and will disintegrate as guest CO₂ molecules diffuse out of hydrate cages into the water. The implication of

(4) and (5) is that, while small volumes of water injected into a larger liquid CO₂ reservoir may be completely converted into stable hydrates, the reverse process (liquid CO₂ released into a larger volume of water) will result only in a thin interfacial hydrate layer that undergoes a continuous cycle of collapse and regeneration. Tests also have revealed that the hydrate surface has an affinity for other like surfaces (possibly due to the presence of broken hydrogen bonds) and will rapidly attach itself and fuse on contact.

While certain issues, such as stability limits (i.e., what constitutes a saturated sea water phase for the three component hydrate-liquid CO₂-water system), catalysis, and kinetic rate constants, continue to generate discussion, there appears to be sufficient information at present on CO₂ hydrates to proceed with a field experiment and local discharge model development. One topic that may warrant additional rig tests is hydrate fouling of submerged disposal pipelines and injectors.

Single Droplet Dissolution

The liquid CO₂-sea water system is hydrodynamically unstable (Teng *et al.*, 1996a) and under most practical discharge scenarios, the effluent CO₂ will break-up to form droplets. The rate at which these droplets dissolve may have serious environmental and long-term containment implications, particularly for situations involving release at depths where buoyancy will transport the droplets vertically through the water column.

Laboratory studies of single CO₂ droplet dissolution have been conducted in quasi-static (Aya *et al.*, 1992; Fujioka *et al.*, 1994) and moving (Aya *et al.*, 1993; Hirai *et al.*, 1996) water environments and have examined the effects of hydrate films, ambient pressure and temperature, approach water velocity, and CO₂ content of the water. In all cases, the droplets were bled into a pressurized water test cell and restrained with mechanical barriers. Droplet shrinkage was monitored with video cameras and image analysis yielded quantitative data on the change of droplet diameter as a function of time. Results of these studies are summarised in Table 1.

Table 1 Single CO₂ Droplet Dissolution Results

Investigation	Press. [MPa]	Temp. [K]	Water Velocity [cm/s]	Initial Diameter [mm]	Final Diameter [mm]	Diameter Shrinkage Rate [m/s]	Comments
Aya <i>et al.</i> (1992)	5.5	283-293	~ 0	25 - 30	< 10	0.39 x 10 ⁻⁶ (w/hydrate) 8.5 x 10 ⁻⁶ (no hydrate)	
Fujioka <i>et al.</i> (1994)	28 & 35	280	~ 0	13 - 15	~ 3	0.5 x 10 ⁻⁶ (w/hydrates)	fresh water used in tests; some free convection
Aya <i>et al.</i> (1993)	~ 30	274-285	2 - 3	6 - 8	~ 0	0.5-1.5x10 ⁻⁶ (w/hydrate) ~1.6 x 10 ⁻⁶ (no hydrate)	minimal shrinkage of hydrate-encased drop observed in water w/7% mass dissolved CO ₂
Hirai <i>et al.</i> (1996)	9.8-39.2	276-286	1.5 - 7	~ 9	~ 7	0.4-1.9x10 ⁻⁶ (w/hydrate) 1.3-3x10 ⁻⁶ (no hydrate)	fresh water; shrinkage rates inferred from data; initial dia. only reported for 2 cases

There is a reasonable level of agreement between data from the four cited investigations; variations probably can be ascribed to differences in test conditions. At temperatures and pressures that foster formation of a hydrate film, the diameter of CO₂ droplets appear to decrease at rates between 0.4 and 1.9 $\mu\text{m/s}$. Experiments also confirm the anticipated result that a solid hydrate film at the CO₂-water interface inhibits mass transfer.

One major shortcoming of the early investigations was that they were unable to account for convective effects, which are expected to be significant at intermediate depths where maximum buoyant velocities of millimetre- to centimetre-size liquid CO₂ droplets will be of the order of 10 cm/s. Hirai *et al.* (1996) addressed this issue in their study and concluded that the rate of mass transfer scales as the square root of the relative velocity of the droplet and ambient water. Although not reported, it can be inferred that their data covers a range of Reynolds numbers (based on diameter) extending from about 50 to 500, which corresponds to flow around buoyant droplets in the 2–10 mm diameter range at 1000 m depth.

Similar trends were observed by Aya *et al.* (1993) and by Hirai *et al.* (1996) when water temperature was varied. Shrinkage rates of hydrate-covered droplets increased by about a factor of three between 274 K and 284 K. Droplets without a hydrate film were essentially unaffected by temperature in this range. Hirai *et al.* also noted an increase in shrinkage rate with pressure.

Over the past five years, laboratory experiments have produced important data on single droplet dissolution. As in the case of hydrate studies, this class of investigation is relatively mature: although a number of issues must still be resolved, there appears to be sufficient information available to proceed with local discharge model development and to pursue the design of a field test. Three areas which may warrant additional study are: (1) the effect of dissolved CO₂ content and salinity on droplet mass transfer; (2) the influence of mechanical restraints on measured shrinkage rates; and (3) flow field turbulence effects.

Aya *et al.* (1993) observed that the rate of reduction of the diameter of a hydrate-covered droplet varied as $C^{3.5}$, where C is the concentration of dissolved CO₂ in the water phase. Conventional practice has the shrinkage rate varying linearly with C (Hirai *et al.*, 1996). The apparent power-law mass transfer behavior must be confirmed since it has important modelling implications and may profoundly influence the structure of practical discharge plumes in regions of the flow where high droplet density and low entrainment/dilution prevail. Warzinski *et al.* (1997), have remarked that droplet shrinkage rates appear to be noticeably lower in sea water than in fresh water. This effect also can be detected in the data of Aya *et al.* (1993). Since the other cited studies have employed fresh water, it would be worthwhile to conduct a few more sea water experiments to supplement the existing database and to quantify this effect.

Warzinski *et al.* (1997) also note that hydrate formation on the surface of CO₂ droplets is facilitated by contact with some surfaces. This type of 'catalysis' was reported earlier in a number of studies (North *et al.*, 1993). Since all experiments in Table 1 utilized mechanical restraints to immobilize the shrinking droplets for observation, their results may be influenced to a degree by this phenomenon. Assuming that the hydrate film on a droplet undergoes a continuous cycle of collapse and regeneration (Teng *et al.*, 1996b), the presence of a restraining surface may alter this cycling and, hence, the rate of mass transfer. A rig study that will address these concerns by monitoring dissolution without artificial restraints is underway (Masutani, 1996).

Finally, since practical discharge scenarios may generate dense effluent plumes where droplets move in the wakes of other droplet (or in the wake of a moving disposal pipeline) and can encounter small scale ocean turbulence, the influence of water phase turbulence on mass transfer should be investigated through appropriate laboratory experiments.

Diagnostic Development

Uchida and his co-workers (Uchida *et al.*, 1997) have led the development of laser Raman methods to detect and to quantify dissolved CO₂ and CO₂ hydrate levels in water. Masutani *et al.* (1995) have reported a similar study. Nishio *et al.* (1993) characterised the performance of an optical two-color absorption technique to monitor solution pH using Bromothymol Blue and Methyl Red indicators. Ohsumi and his co-workers at the Central Research Institute of the Electric Power Industry (CRIEPI) of Japan reportedly have developed and patented a robust, fast time response pH probe based on an IS-FET (Ion Sensitive Field Effect Transistor) sensing element (Ohsumi, 1996).

The aforementioned work represents the bulk of effort applied to date to devise diagnostics for CO₂ ocean disposal studies. This research area has received much less attention than hydrates and droplet dissolution, since the need for sophisticated instrumentation has been modest up to this point. Visual observation by means of video cameras has been the predominant method of collecting information in the laboratory. Modelling and engineering activities, however, will require more quantitative data in the future and field tests will demand instruments that can be deployed and operated in the hostile environment of the deep ocean. To meet these needs, additional resources must be committed to diagnostic development.

Two near-term priority items are: (1) instruments to monitor (scalar) contaminant levels and fluid velocities during field experiments; and (2) a non-intrusive diagnostic to perform temporally- and spatially-resolved measurements of CO₂ clathrate hydrate concentrations in the laboratory. Regarding item (1), scalars of interest include solution pH and dissolved CO₂ concentration, solution density, and CO₂ droplet number density and size spectra. Techniques which could provide instantaneous maps of the scalar fields would be preferable to point-measurement methods, since deployment and operation of multiple sensors would be cumbersome in the ocean. Aside from video methods (optical scattering) which would only yield the location of the dispersed droplet phase, diagnostics which exploit differences in the density of the sea water and contaminant and contaminant-enriched water may offer some opportunities. Optically, this could involve shadowgraph or Moiré deflectometry, although the small variations in the index of refraction which are anticipated and scattering by droplets and particles may render these approaches unfeasible. Acoustic methods (sonar) should be easier to implement; however, spatial resolution may be poor and once again only the droplet phase will be imaged well.

A number of options exist to perform measurements of velocity in the field. Point data can be obtained with simple and inexpensive pitot probes (which unfortunately are insensitive to low flow velocities) or anemometers. For sensitive, high-bandwidth measurements, fiber LDV (Laser Doppler Velocimetry) probes or acoustic Doppler probes are available, albeit at a price. It should be possible to apply the principles of PIV (Particle Image Velocimetry) to map the instantaneous velocity field, provided that the imaged area of the flow is not too large.

Injection Dynamics

Early in the development of the ocean storage strategy, several alternatives emerged which proposed discharging pure liquid CO₂ directly into the deep ocean from a submerged conduit. As a result, researchers were anxious to determine how CO₂ effluent would behave when injected into cold, high-pressure sea water. Aya & Yamane (1991) performed an experiment in which small batches of liquid CO₂ were pumped into a 5 cm diameter x 200 cm height cylindrical pressure vessel filled with fresh or sea water at about 5°C and 7 MPa. The CO₂ was introduced both through a tube and a sintered metal diffuser. Video was recorded through viewports.

The CO₂ was observed to form a distinct dispersed phase. When injected through the tube, droplets were produced which often agglomerated. At very low discharge rates, the interfacial

hydrate layer formed cylindrical structures similar to those observed around hydrothermal vents by Sakai *et al.* (1990). A hydrate 'snow' was generated using the sintered metal.

The principal shortcoming of Aya's facility and another small flow reactor employed by Nishikawa and his co-workers at Tokyo Electric Power Company and IHI (Nishikawa *et al.*, 1992) was the inability to simulate the dynamics of continuous injection at reasonable flow rates. Moreover, while the flow visualisation images which were obtained in those studies provided new qualitative understanding of injection phenomena, current modelling and field test engineering tasks demand quantitative data on droplet size spectra and on fluid and dispersed phase velocities. Investigations which quantify injection dynamics therefore are a priority item.

Masutani *et al.* (1993) devised an experiment to address some of the needs identified above. Their large cylindrical pressure vessel has an internal volume of approximately 0.56 m³ (560 l) and its CO₂ delivery system can sustain continuous liquid injection rates of up to 0.27 kg/s. Water temperatures and pressures may be adjusted to simulate the ocean depths down to 600 m. For discharge orifices with diameters up to about 1 cm, a range of conditions extending from creeping to fully turbulent jet flow may be examined.

Under sponsorship from the U.S. Department of Energy and ABB Management, experiments are underway to quantify scalar and streamwise velocity fields in the region immediately downstream from an injector (Masutani, 1996). Utilizing a modified PDPA (Phase Doppler Particle Analyser), simultaneous, spatially and temporally resolved measurements of CO₂ droplet and fluid velocity, droplet size, and droplet number density are being performed as discharge velocity, injector orifice size and geometry, and simulated depth are varied.

Droplet Interactions

In the experiments of Aya & Yamane (1991), Hirai (1997) and Teng and his co-workers (Teng 1996), CO₂ droplets produced by injection into water were observed to agglomerate on contact. The hydrate film encasing the droplets appears to prevent complete coalescence. Teng *et al.* (1996a) suggest that agglomeration is facilitated by 'broken' hydrogen bonds at the hydrate surface.

During actual discharge in the ocean, droplet agglomeration and other interactions may strongly affect CO₂ dissolution and dispersion. Droplet clusters will have unusual drag characteristics and more surface area (which affects mass transfer rates) than a spherical droplet of the same volume. At high loadings, droplets will move and dissolve in the velocity and concentration wakes of other droplets.

Information currently available on droplet interactions is limited to a few video records. Additional work in this area is being planned by Teng and his co-workers at the National Institute of Materials and Chemical Research (Japan), by Hirai and his group at the Tokyo Institute of Technology, and by Masutani and his co-workers at the University of Hawaii. In consideration of the importance of this subject, particularly with regard to local discharge model development, laboratory investigations of CO₂ droplet interactions should be given high priority. Several questions which must be answered include: (1) can the hydrate film between agglomerated droplets break down, leading to complete coalescence; (2) how is agglomeration affected by relative velocity (of two droplets), geometry (trajectory), and relative size of the collision partners; and (3) is the surface area of agglomerated droplets a random quantity or is there a statistically-most-likely surface-to-volume ratio? Many of these questions can be addressed using existing rigs and fairly simple diagnostic techniques such as video capture and quantitative image analysis.

Droplet Plumes in Stratified Media

In many direct release scenarios, the CO₂ is expected to form a plume that entrains sea water while penetrating through the stably stratified water column and periodically shedding (peeling) dense fluid (Liro *et al.*, 1992; Reingold, 1994). These plumes will be subject to currents and ocean turbulence. The hydrodynamics of this type of droplet plume are poorly understood and ongoing modelling efforts suffer from a lack of applicable experimental data. Insufficient understanding of the behavior of these plumes also complicates the design of a field experiment, since, among other things, the measurement grid (i.e., the selected measurement area in the ocean) cannot be optimised.

Laboratory investigations that can provide data on droplet plume dynamics in stratified media must be conducted to sustain modelling activities and preparations for a field test. These investigations do not need to be performed in a pressurised rig but should be pursued in a water tunnel that is large enough to allow for multiple peels and which can simulate the effects of currents and turbulence. Quantitative measurements of axial and radial velocities and scalar concentrations are desired, preferably supplemented by flow visualisation. A number of validated fluid mechanics measurement techniques are available for these purposes.

To date, only a few preliminary experiments have been conducted by the MIT group in a small tank with limited plume rise height (Reingold, 1994). A more comprehensive experiment has been proposed (Herzog, 1996) that would address most of the needs mentioned above.

RECOMMENDATIONS AND SUMMARY

Laboratory rig experiments can be applied effectively to investigate near-field phenomena relevant to local discharge models and to resolve engineering and operational concerns related to the CO₂ ocean storage concept. Rig experiments cannot, however, provide information on long time-scale, far-field transport processes in the ocean needed to support mesoscale and OGC modelling efforts to predict the term of containment.

At the current stage of development, rig experiments should be conducted to: (1) validate underlying principles of operation of proposed disposal techniques; (2) support development of local discharge models; (3) simulate operation of various components of a disposal process; (4) support the design and implementation of field experiments; and (5) develop diagnostics for applications in the field or to meet critical measurement needs in the laboratory.

Laboratory rig studies of issues directly related to the CO₂ ocean storage concept have been pursued for less than a decade. In that time, significant advances have been made, particularly in the areas of hydrate formation kinetics and single CO₂ droplet dissolution. Investigations of those topics are fairly mature and, hence, related deficiencies in understanding which persist are not expected to hinder model development or the pursuit of a field disposal experiment.

Development of diagnostics for application in the laboratory or in the ocean has received much less attention than hydrates and droplet dissolution studies. Activities must be intensified hereafter to devise robust instruments for field disposal tests that can be used to monitor contaminant levels and fluid velocities.

In addition to diagnostic development, it is recommended that the following laboratory research topics be assigned high priority in the near-term: (1) buoyant droplet plumes in stratified media; (2) CO₂ injection dynamics; and (3) multiple droplet interaction phenomena. Studies of hydrate fouling of pipelines and injectors should also be initiated, since these problems are relevant to the field experiment.

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